

## High light intensity effects on nanoscale open-circuit voltage for three common donor materials in bulk heterojunction solar cells

Yuan Zhang, Xuan-Dung Dang, Martijn Kuik, Sarah R. Cowan, Peter Zalar, Chunki Kim, and Thuc-Quyen Nguyen\*

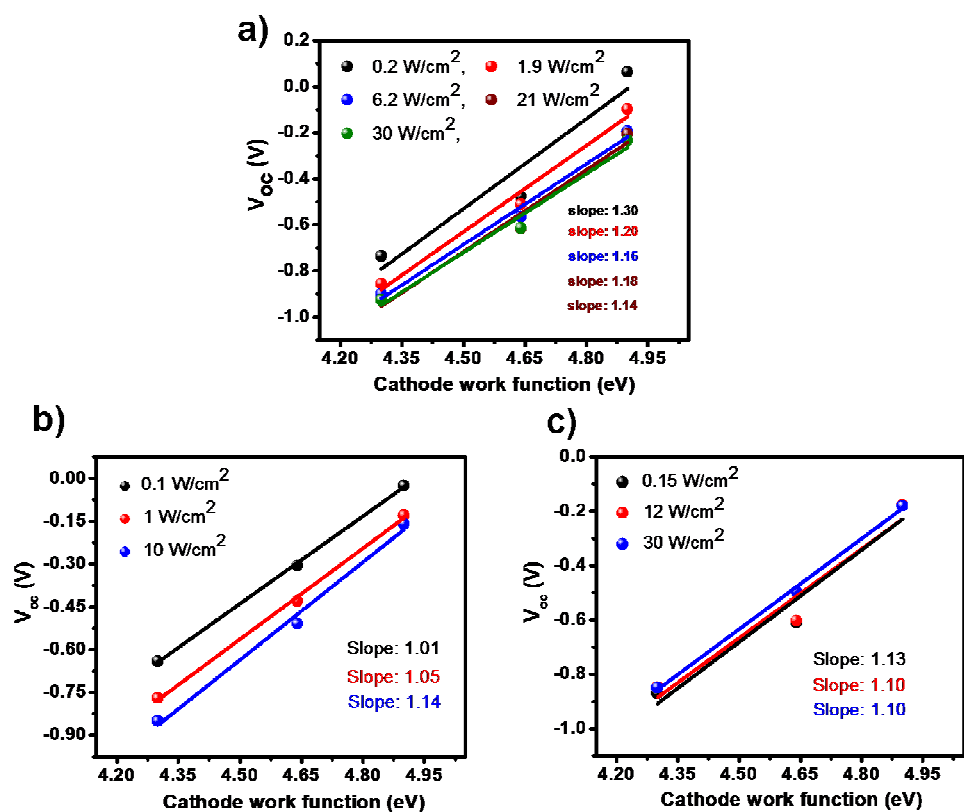
*Department of Chemistry and Biochemistry and Department of Physics, University of California at Santa Barbara, Santa Barbara, CA 93106, USA.*

### Supplementary Information

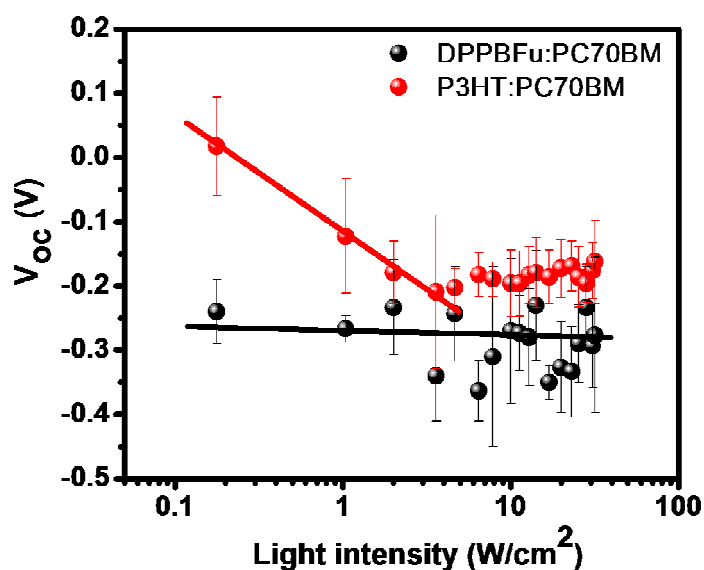
**ITO substrates modification:** The work function (*WF*) of indium-tin oxide substrates (ITO, Thin Film Devices, Inc.) was modified by surface treatment following the procedures reported elsewhere.<sup>[1,2]</sup> Regular ITOs were cleaned by sonication sequentially in deionized water, acetone and isopropanol. Activated ITO substrates were prepared by cleaning ITOs with sonication in isopropanol for 15 min, followed by a soaking procedure in H<sub>2</sub>O:NH<sub>3</sub>:H<sub>2</sub>O<sub>2</sub> (5:1:1 by volume) solution for 15 min. A 30 % ammonium hydroxide (NH<sub>3</sub>) and a 28 - 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) were used as received. 3-aminopropyltrimethoxysilane (APTMS, Sigma-Aldrich) was self-assembled on activated ITO substrates from a methanol solution of 1 % (v/v) APTMS for 1 hour. The APTMS-modified ITOs were then washed with methanol and dried by nitrogen before use. The *WF* of ITO/PEDOT:PSS, activated-ITO, and APTMS-ITO is 4.90 eV, 4.64 eV and 4.30 eV, respectively as measured by ultraviolet photoelectron spectroscopy (UPS).<sup>1</sup>

**Film preparations:** Films of P3HT:PC<sub>70</sub>BM (55:45, by weight), DPP(TBFu)<sub>2</sub>:PC<sub>70</sub>BM (60:40), and PCDTBT:PC<sub>70</sub>BM (1:4) were spin-cast from a 1.8 % (w/v) chloroform solution, a 1.8 % (w/v) chlorobenzene, and a 3.5 % dichlorobenzene:chlorobenzene (DCB:CB, 1:3 by volume) solution mixture, respectively (spin-rate: 2000 rpm). The P3HT:PC<sub>70</sub>BM and DPP(TBFu)<sub>2</sub>:PC<sub>70</sub>BM films were then annealed at 110 °C and 150 °C for 15 minutes in a nitrogen-purged glove box. The samples after annealing were directly transferred to a nitrogen-flow cell for photoconductive atomic force microscopy (pc-AFM) measurements.

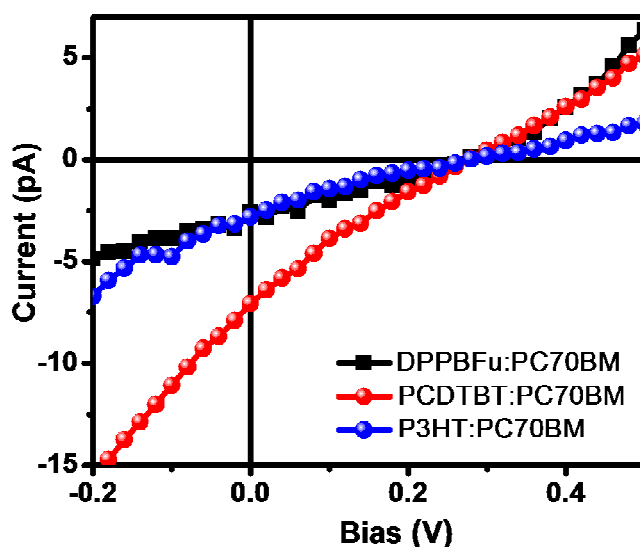
**pc-AFM measurements:** pc-AFM was measured under white light illumination from a Xe lamp source. The light was focused on the sample surface by using a 60× objective (Olympus, LUCPLFLN60X) with a light spot size of ~160 μm in diameter. The total optical power incident on the sample was measured by a Newport 842-PE power meter with 818-series calibrated photodiode head. The light intensity was adjusted by an iris window and calibrated before the measurement. We assume that the optical distribution is homogeneous in the spot center and the AFM tip sits in the center of the focused light area. To calibrate the digital-to-analog (DAC) converter offset, we applied the testing procedure described by Ginger and coworkers.<sup>[3]</sup> A 1 GΩ resistor was connected in series between the current/voltage source and the AFM chip holder/preamp. A DAC offset of -114 mV was applied based on the obtained X-intercept of collected *I*-*V* curves. In order to avoid damages of device surfaces, the topography and current images were mapped at a minimized contact force of about 7 to 10 nN as controlled by optimizing the deflection set-point. To get a stable contact and reproducible data, the *I*-*V* curves were collected at a contact force of 50 nN.



**Fig. S1.**  $V_{oc}$  attained by pc-AFM as a function of cathode WF under various light intensities for (a) P3HT:PC<sub>70</sub>BM, (b) PCDTBT:PC<sub>70</sub>BM, and (c) DPPBFu:PC<sub>70</sub>BM. The lines are the linear fittings to data.



**Fig. S2.** Light intensity-dependent  $V_{oc}$  by pc-AFM for P3HT:PC<sub>70</sub>BM and DPP(TBFu)<sub>2</sub>:PC<sub>70</sub>BM using APTMS-ITO substrates and a Ag tip.



**Fig. S3.** Current-voltage characteristics of the three BHJs using ITO/PEDOT substrates and a Ag tip under a light intensity of 300 sun.

1. X.-D. Dang, A. B. Tamayo, J. H. Seo, C. V. Hoven, B. Walker, and T.-Q. Nguyen, *Adv. Funct. Mater.* 2010, **20**, 3314.
2. X.-D. Dang, A. Mikhailovsky, and T.-Q. Nguyen, *Appl. Phys. Lett.* 2010, **97**, 113303.
3. O. G. Reid, H. Xin, S. A. Jenekhe, and D. S. Ginger, *J. Appl. Phys.* 2010, **108**, 084320.